



Process and product synthesis/design

Design of green diesel from biofuels using computer aided technique

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ABSTRACT

This paper presents a systematic computer aided technique to design a sustainable (safe, environmentally friendly and economical) tailor-made “green diesel” blend that satisfies a set of desirable target properties. In this work, the software, Integrated Computer Aided System (ICAS) was used to predict the green diesel properties. The blending model is formulated to identify a set of feasible mixture blends that satisfy the desirable target properties such as density and viscosity. The blend design problem is formulated as an NLP problem and solved through GAMS. Application of the systematic technique yields several promising green diesel blends. Four final candidate blends were selected based on three key criterion, i.e. cost, sulfur content and carbon dioxide emissions. The results show that the best diesel contains 82.4% diesel, 16.6% butanol and 1% butyl levulinate. This diesel blend contributes to the reduction of CO₂ emission and sulfur content by up to 15% and 17%, respectively.

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1. Introduction

Nowadays, biofuel from biomass has become an important alternative source of energy. Compared to fossil fuel, biofuel is almost CO₂ neutral and is therefore capable of reducing carbon dioxide emissions that is the main cause of global warming. Biomass-derived fuels also have negligible sulfur content and therefore, do not contribute to the emissions of sulfur dioxide which causes acid rain (Ashok, 2009). Adding a percentage of biofuel which acts as an additive and emulsifier into diesel could improve the fuel performance. As an example, palm-oil derived biodiesel can be used as an effective emulsifier for diesohol emulsions (Kraipat, Monpilai, & Juthawan, 2006). Various sources of biofuels including ethanol, butanol and alkyl esters which include ethyl levulinate and butyl levulinate can be mixed with diesel in the right proportion without significant modifications to the engine.

Generally, ethanol can be blended with diesel with no engine modifications required (Ajav & Akingbehin, 2002). Recently, butanol was reported to be able to further improve the fuel properties of the blends since butanol has a higher solubility in diesel as compared to ethanol (Murat Karabektas & Murat Hosoz, 2009). Diesel–methyl ester blends contain fuel properties that are very close to the conventional diesel fuels at low concentrations of up to 20% methyl esters (Ertan & Mustafa, 2009). Currently, methyl ester is used as a fuel additive. On the other hand, butyl levulinate

(BL) was found as one of the alkyl esters that was reported to have potentially interesting fuel additive characteristics.

As there are many types of biofuels that can be blended with diesel, there is a need for a tool to assess the effectiveness of biofuel blends in terms of economy, safety and sustainability. The blend can consist of one or more types of biofuel with diesel. Experimental methods have been commonly used to find the best biofuel blend. This method is however time consuming and costly because of the need to do trial and error tests on many samples experimentally. Nowadays, computer aided technique can reduce the time needed to solve these product design problems while experiments could be done once a short list of promising candidates have been identified.

Computer aided methods can be used to identify the best ratio of fuel blends by significantly narrowing down the search space to determine the promising candidate fuel blends. In this paper, by using a computer aided technique, three biomass feedstocks, i.e. ethanol, butanol and butyl levulinate are evaluated to find the optimum diesel–biofuel blend. The ultimate objective is to create a tailor-made green diesel that can become a viable alternative to fossil fuel to help prolong the fossil-based diesel supply availability.

2. The blend design methods

There are some researches done to analyse the effect of biofuel to the properties of diesel blend such as kinematic viscosity, heating value, density, calculated cetane index, cloud point and distillation temperature (Pedro, John, & Adres, 2008). Research done by Ertan and Mustafa (2009) is to characterize the key fuel properties of the blends such as density, viscosity, pour point, distillation temperatures and flash point by blending methyl ester with diesel.

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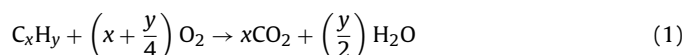
There is also a research focused on the properties that influence the injection and engine characteristic significantly, which need to be investigated through experiments. The physical and chemical properties include density, cloud point, pour point, kinematic viscosity, flash point, cetane index and lubricity (Eloisa et al., 2011). In this paper, the fuel blends were characterized by predicting their viscosity, density, distillation temperature and cetane number.

Kinematic viscosity is one of the most important fuel properties because it has effects on the atomization quality, the size of fuel drop and the penetration. Therefore, it influences the quality of combustion. Low quality can cause leakage in the fuel system, while high viscosity causes poor fuel atomization and incomplete combustion, increases the engine deposits, need more energy to pump the fuel and wears fuel pump elements and injectors (Ghobaian, Rahimi, Hashjin, & Khatamifar, 2008).

Density is a property which directly affects the engine performance characteristics and the efficiency of fuel atomization (Ryan, Dodge, & Callahan, 1984). Many performance characteristics such as cetane number and heating value are related with density (Tat & Van Gerpen, 1999).

Distillation temperature includes the determination of the range of boiling points for the fuels and is used to characterize the fuel in terms of the boiling temperatures of its component. The distillation range of the diesel fuel affects the fuel properties such as viscosity, flash point and density (Ertan & Mustafa, 2009). In this paper, the fuel blends were characterized by predicting their viscosity, density, distillation temperature and cetane number.

Generally, the stoichiometric burning of hydrocarbon diesel in oxygen is given by Eq. (1).



Note from Eq. (1) that diesel with a molecular formula $C_{16}H_{34}$ produces 3.11 g CO_2 per gram fuel, while the CO_2 emission is assumed to be zero for bio-fuels. Mixtures which are cost-competitive and emit less CO_2 as well as SO_2 are considered as the final candidates.

For miscibility analysis of biofuel and diesel, at room temperature, with concentration of 99.5% ethanol, the intersolubility of ethanol and diesel was not limited. They could be mixed into a homogeneous solution at any ratio (Prommes, Apanee, & Samai, 2007). A research done by Areerat, Apanee, and Samai (2009), the use of butanol in diesohol could solve the problem of fuel instability at low temperatures because of its higher solubility in diesel fuel. For butyl levulinate, from Material Safety Data Sheet (MSDS), one of the basic properties of Butyl levulinate is being soluble in oil, ethanol, ether, chloroform and other organic solvents (<http://www.guidechem.com/products/2052-15-5.html>, access on 18th August 2011, <http://www.un.org/esa/gite/cleanfuels/asia.pdf> access on 18th August 2011, <http://www.guidechem.com/products/2052-15-5.html>, access on 18th August 2011). Alternatively, the miscibility of the candidate bio-fuel with diesel could be predicted with a suitable property model or verified experimentally.

A systematic methodology for designing a chemical mixture or a blend has been modified from Gani (2004). It consists of four steps as shown in Fig. 1. The first step involves specifying the target properties and their values. Next, the possible mixture alternatives are generated using computer aided mixture/blending technique. Property models to predict all the target properties for a mixture are from (Pedro et al., 2008). The third step involves screening of several promising alternatives to meet the set of target properties (Ng, Gani, & Johansen, 2007). Generalized Algebraic Modeling System (GAMS) programming is used to generate the possible mixtures which satisfy the target properties. Finally, the best candidate is selected from among the shortlisted candidates based on three

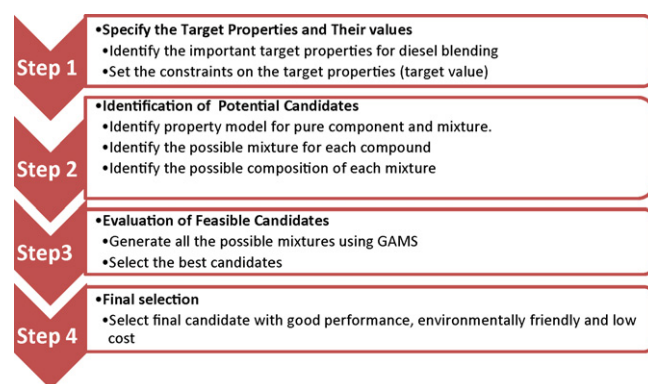


Fig. 1. Overall methodology for fuel mixture/blend design.

Table 1

Properties of raw materials for diesel blending.

No.	Properties	Butanol	Diesel	Butyl levulinate	Ethanol
1	Viscosity (cSt)	3.64	4.0	4.5	1.52
2	Density (kg/cm ³)	932	823	1091	795
3	Distillation temperature (T95) (°C)	165	376	238	78.2
4	Cetane number	25	49	48	8
5	Cost of raw material (USD/L)	9.02	0.60	70.84	0.43

Properties of diesel from Choo, Young, et al. (2005). Properties of butyl levulinate from property prediction in ICAS.

main criteria such as cost, emission reduction and sulfur content of the new green diesel.

2.1. Specify the target properties and their targeted values

In the case of fuel blending, several important fuel properties should be considered. These include density, viscosity, distillation temperature and cetane number. The properties of butanol, ethanol, diesel and butyl levulinate are given in Table 1. The data are obtained from literature and from the database of the ICAS software. For pure components, property prediction models from ICAS (Gani, Hytoft, & Jacksland, 1997) are used to predict the necessary property values for butyl levulinate (such as viscosity, density and distillation temperature) and diesel (refractive index, density and molecular weight). Prediction of the target properties is based on the molecular structure of each component. Cetane number of butyl levulinate is predicted using the model of Gopinath, Puan, and Nagarajan (2009). The target properties for the more established components like butanol and ethanol are taken from the literature.

The next step is to set the target values for the target properties. The target values were set in the form of lower and upper bounds for each target property. The target value is the starting point for all the design steps. The design result is influenced by the target values settled in this task. Table 2 gives the ranges of target properties required for diesel blending that can satisfy the diesel engine performance without modification.

Table 2

Ranges of the desirable target properties.

Properties	Biofuel target properties range
Viscosity (mm ² /s @ cSt)	2.0–4.5
Density (kg/m ³)	820–860
Distillation temperature, T95	Up to 360 °C
Cetane number	45–50

Target properties for viscosity, distillation temperature and cetane number from Konstantinos, Stella, Vasiliki, and Petros (2010).

2.2. Identification of potential green diesel candidates

2.2.1. Pure and mixture property models for the green diesel

In order to solve the blending problem, suitable property models are needed. In this study, two mixture property models were used to predict the target properties of the green diesel blend. The first model is the Kay's Mixing Rule (Eq. (2)) that was used to predict the cetane number, distillation temperature, density, and sulfur content of the tailor-made green diesel. The second model was the Arrhenius Mixing Rule (Eq. (3)) that was used to predict the viscosity (Pedro, John, & Adres, 2008). On the other hand, three pure property models were derived from the literature (Eqs. (4)–(6)). Eq. (4) is used to predict sulfur content of pure diesel (Mohammad, Razi, Nasrin, & Yousef, 1999). For biofuels, the sulfur content is assumed to be zero. Eqs. (5) and (6) are used to predict the parameters of Eq. (4).

1. Kay's mixing rule

$$\varphi_B = \sum_i^n x_i \varphi_i \quad (2)$$

where: x_i is the mass fraction of i th component, Φ_B is the property of blend fuel, Φ_i is the property of i th component.

2. Arrhenius mixing rule

$$\ln \mu_B = \sum_i^n x_i \ln \mu_i \quad (3)$$

where: μ_B is the absolute viscosity of the blend, μ_i is the absolute viscosity of pure i th component.

3. Sulfur content for pure diesel:

$$S\% = -58.02 + 38.4628RI - 0.0229m + 22.45G \quad (4)$$

where: $S\%$ is the sulfur weight percentage of the diesel, RI is the refractivity intercept defined by Eq. (4), m is the parameter defined by Eq. (5), SG is the specific gravity of the diesel at 15.5 °C.

$$RI = n - \frac{d}{2} \quad (5)$$

where: RI is the refractivity intercept, n is the refractive index of diesel, d is the liquid density of diesel

$$m = M(n - 1.475) \quad (6)$$

where: m is the parameter defined by Eq. (5), M is the molecular weight of diesel, n is the refractive index of diesel.

2.2.2. NLP formulation for tailor-made diesel blending

In this work, the objective function is to identify a set of feasible candidate blends that satisfy the desirable target properties. Eq. (7) represents the gross economic potential of tailor-made green diesel, taking into account the value of green-diesel and the cost of raw materials used without considering the biofuels production cost. Eqs. (8)–(10) are used to calculate the density, distillation temperature (T95) and cetane number. Arrhenius equation is used to calculate the viscosity of the mixture (Eq. (11)). The amount of carbon dioxide (Eq. (12)) released by each diesel blend is calculated from the mass fraction of diesel and emission factor of the diesel with the assumption of zero CO₂ emission from biofuels.

Six types of variables are first defined, continuous variables, $z(j)$, $x(i,j)$, $\text{density}_{\text{mix}}(j)$, $\text{viscosity}_{\text{mix}}(j)$, $\text{CN}_{\text{mix}}(j)$, $\text{DT}_{\text{mix}}(j)$ and $\text{CO}_2(j)$ representing the production cost, mass fraction of each compound, mixture density mixture viscosity, cetane number of mixture, distillation temperature of mixture, and emissions of carbon dioxide, respectively. A complete description of the NLP formulation is discussed below.

The objective function of this work is to minimize the total fuel cost.

$$Z_j = \sum_i x_i \times C_i \quad (7)$$

where: Z_i is the cost of green diesel fuel, C_i is the cost of each compound (USD/L), x_i is the mass fraction of each compound.

The minimization of objective function represented by Eq. (7) is subjected to the following constraints:

(a) Density of the mixture

The density of the mixture, $\text{density}_{\text{mix}}$ is obtained using Kay's rule by multiplication of mass fraction of each compound with density of pure chemical (kg/m³)

$$\text{density}_{\text{mix}} = \sum_i x_i \times \text{density}_i \quad (8)$$

(b) Distillation temperature of the mixture

The distillation temperature of the mixture (°C) is calculated using Kay's rule as well by multiplication of mass fraction of each compound with distillation temperature of pure chemical (°C).

$$\text{DT}_{\text{mix}} = \sum_i x_i \times \text{DT}_i \quad (9)$$

(c) Cetane number of the mixture

Cetane number of the mixture, CN_{mix} is defined according to Kay's rule by multiplication of mass fraction of each compound with cetane number of pure chemical, CN_i .

$$\text{CN}_{\text{mix}} = \sum_i x_i \times \text{CN}_i \quad (10)$$

(d) Viscosity of the mixture

Viscosity of the mixture is calculated using Arrhenius Mixing Rule and given by

$$\ln v_{\text{mix}} = \sum_i^n x_i \ln v_i \quad (11)$$

where: v_i is the viscosity of pure chemical (cSt), v_{mix} is the viscosity of mixture (cSt).

(e) CO₂ emissions

Amount of CO₂ emissions released from the mixture can be calculated using equation below,

$$\text{CO}_{2j} = \left(\frac{3.11 \times \text{density}_{\text{mix}j} \times x_{\text{diesel},j}}{1000} \right) \quad (12)$$

where: CO_{2j} is the amount of carbon dioxide release from mixture (kg CO₂/L), $x_{\text{diesel},j}$ is the mass fraction of diesel in mixture.

The target properties for density, cetane number, viscosity and distillation temperature for the mixture must satisfy the acceptable range as shown below,

Properties	Lower limit	Upper limit
Density	820	860
Cetane number	40	50
Viscosity	2.0	4.5
Distillation temperature		360

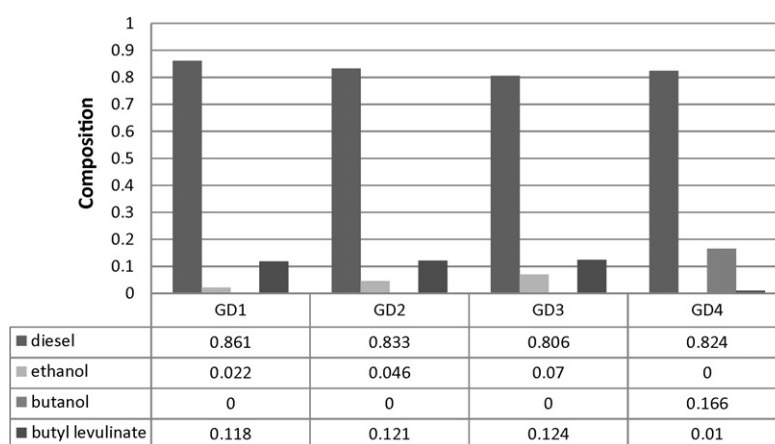
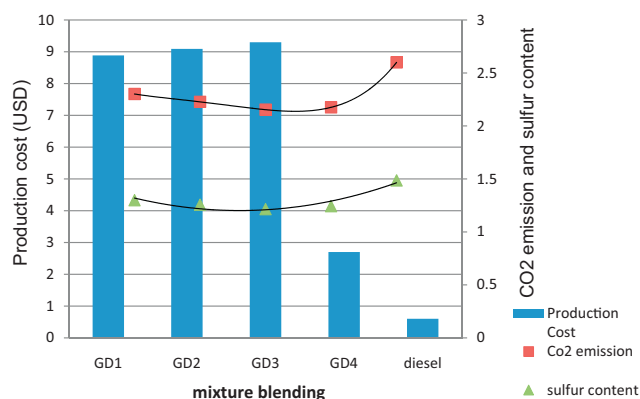
Eqs. (7)–(12) are coded into GAMS to identify the feasible candidates that satisfy the desirable target properties.

3. Results

Table 3 gives the feasible tailor made green diesel (GD) formulations that satisfy the desired target properties. All proposed mixtures consist of at least 15% composition of biofuel in the green diesel. Fig. 2 shows the compositions of raw materials in diesel

Table 3
Properties of mixtures.

Properties	GD1	GD2	GD3	GD4
Composition				
Diesel	0.861	0.833	0.806	0.824
Ethanol	0.022	0.046	0.070	0
Butanol	–	–	–	–0.166
Butyl levulinate	0.118	0.121	0.124	0.010
Viscosity (cSt)	4.006	3.914	3.823	3.975
Density (kg/m ³)	860.00	860.00	860.00	849.61
Distillation temperature (°C)	309.44	303.15	296.87	297.52
Cetane number	48	47	46	45
Production cost (USD/L)	8.89	9.09	9.306	2.70
Carbon dioxide emission (kg CO ₂ /L)	2.302	2.228	2.154	2.176
Sulfur content (%)	1.299	1.257	1.215	1.243
Percentage of CO ₂ emission reduction (%)	10.8	13.69	16.55	15.70
Percentage of sulfur content reduction (%)	14	16.75	19.54	17.68

**Fig. 2.** Formulation of tailor made green diesel.**Cost, sulfur content and carbon dioxide emissions for diesel and each type of fuel blend****Fig. 3.** Cost, sulfur content and carbon dioxide emissions for diesel and each type of fuel blend.

blends. GD 1, 2, and 3 consists of diesel, ethanol and butyl levulinate at different compositions. On the other hand, GD 4 consists of diesel, butanol and butyl levulinate.

4. Discussion

In selecting the best green-diesel candidate, the cost, emission of sulfur dioxide as well as carbon dioxide are the three main factors considered. Fig. 3 illustrates the correlation between cost, sulfur content and carbon dioxide emissions for diesel and the four

possible types of green diesel. GD3 produces the lowest carbon dioxide emission because the mixture contains the lowest composition of diesel (see Fig. 2). However, since GD3 contains 12% of butyl levulinate, the cost of this green diesel is USD 9.30/L which is the most expensive to produce among the 4 mixtures. Note that pure butyl levulinate costs USD70.84/L (the most expensive biofuel used in this study). GD 4 is the most preferable due to its lowest production cost (USD 2.70/L). The carbon dioxide emission produced by GD4 is the second lowest as compared to the emissions produced by other mixture blends. This is a reduction of 15.70% of carbon dioxide emission as compared to the conventional diesel emission. The sulfur content in this new green diesel is 17.68% less compared to that of the conventional diesel.

5. Conclusion

In this study, four promising tailor-made diesel blends that satisfy the desirable target properties of a green diesel have been generated using a computer aided technique. Theoretically, the results show that the most cost-effective, safest and environmental friendly tailor-made diesel contains 82.4% diesel, 16.6% butanol and 1% of butyl levulinate. The modeled mixture is predicted to achieve up to 15% CO₂ emission reduction and 17% reduction of sulfur content as compared to the conventional diesel.

The next key step of the research is to validate the results obtained using the computer-aided technique. Experimental tests will be performed on the predicted green diesel formulations in order to find the proven and tested optimum diesel blend that achieves the desired target properties.

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References

- Ajav, E. A., & Akingbehin, O. A. (2002). *A study of some fuel properties of local ethanol blended with diesel fuel*. Ibadan, Nigeria: Department of Agricultural Engineering, Faculty of Technology, University of Ibadan.
- Areerat, C., Apanee, L., & Samai, J. (2009). Utilization of palm oil alkyl esters as an additive in ethanol–diesel and butanol–diesel blends. *Fuel*, 88, 1618.
- Ashok, P. (2009). *Handbook of plant-based biofuels*. Boca Raton, FL: CRC Pr.
- Choo, Y. M., Yung, C. L., Cheng, S. F., Ma, A. N., Chuah, C. H., & Yusof, B. (2005). Key fuel properties of palm oil alkyl esters. *Fuel*, 84, 1717.
- Eloisa, T. J., Marta, S. J., Andreja, G., Irenca, L., Dorado, M. P., & Breda, K. (2011). Physical and chemical properties of ethanol–diesel fuel blends. *Fuel*, 90, 795.
- Ertan, A., & Mustafa, C. (2009). Characterization of the key fuel properties of methyl ester–diesel fuel blends. *Fuel*, 88, 75.
- Gani, R. (2004). Computer-aided methods and tools for chemical product design. *Chemical Engineering Research and Design*, 82, 1494.
- Gani, R., Hytoft, C., & Jacksland, A. K. J. (1997). An integrated computer-aided system for integrated design of chemical processes. *Computers and Chemical Engineering*, 21, 1135.
- Chobaian, B., Rahimi, H., Hashjin, T. T., & Khatamifar, M. (2008). Production of bioethanol and sunflower methyl ester and investigation of fuel blend properties. *Journal of Agricultural Science*, 10, 225.
- Gopinath, A., Puhani, S., & Nagarajan, G. (2009). Relating the cetane number of biodiesel fuels to their fatty acid composition: A critical study. *IMEchE*, 223, 565.
- Konstantinos, K., Stella, B., Vasiliki, K., & Petros, A. P. (2010). On the prediction of properties for diesel/biodiesel mixture featuring new environmental considerations. In *20th European symposium and computer aided process engineering*.
- Kraipat, C., Monpilai, H. N., & Juthawan, P. (2006). Biodiesel as an additive for diesohol. *Asian Journal on Energy and Environment*, 7, 267.
- Mohammad, R., Razi, Nasrin, N., & Yousef, A. R. (1999). Estimation of sulfur content of petroleum products and crude oils. *Industrial & Engineering Chemistry Research*, 38, 4507.
- Murat Karabektas, & Murat Hosoz. (2009). Performance and emission characteristics of a diesel engine using isobutanol–diesel fuel blends. *Renewable Energy*, 34, 1554.
- Ng, K. A., Gani, R., & Johansen, K. D. (2007). *Chemical product design: Toward a perspective through case studies*. Netherlands: Elsevier's Science & Technology.
- Pedro, B., John, A., & Adres, A. (2008). Basic properties of palm oil biodiesel–diesel blends. *Fuel*, 87, 2069.
- Prommes, K., Apanee, L., & Samai, J. I. (2007). Solubility of a diesel–biodiesel–ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel*, 86, 1053.
- Ryan, T. W., Dodge, L. G., & Callahan, T. J. (1984). The effects of vegetable oil properties on injection and combustion in two different diesel engines. *JAOCs*, 61, 1610.
- Tat, M. E., & Van Gerpen, J. H. (1999). *The kinematic viscosity of biodiesel and its blends with diesel fuels*, *JAOCs*(12), 1511.